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PATENT SPECIFICATION



Application Date : Sept. 13, 1932.

No. 25,478/32. 411,860

Complete Specification Left : July 27, 1933.

Complete Specification Accepted : June 13, 1934.

PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Hollow Flexible Articles.

I, FRANK BERNHARD DEHN, M.Sc., Ph.D., A.I.C., Chartered Patent Agent, a British Subject, of Kingsway House, 103, Kingsway, London, W.C. 2, do hereby declare the nature of this invention (which has been communicated to me by Röhm & Haas Aktiengesellschaft, a Joint Stock Company organised under German Law, of Weiterstädterstrasse 42, Darmstadt, Germany) to be as follows:—

The present invention relates to improvements in or relating to the manufacture of hollow flexible articles, such for example as finger stalls, bulbs, ampullæ, teats, tubes, or the like. Such articles have in general been made of rubber.

According to the present invention articles of the kind set forth are formed of solid and elastic wholly or partially polymerised unsaturated organic compounds singly or in admixture and with or without additional substances. In particular the polymerisation products of derivatives of acrylic acid or its homologues or polymerisation products of the acids themselves are employed. These products are stable as regards their strength, have good extensibility and resistance to tearing and the special elasticity required for the manufacture of finger stalls and the like which must make a good fit without producing hurtful pressure through being pressed or drawn on. In particular there may be mentioned acrylic acid and methacrylic acid, their methyl, ethyl, propyl, amyl, phenyl and benzyl esters and their halogen substitution products such for example as chloracrylic acid methyl ester.

In addition to the compounds mentioned above, other substances containing the group $\text{CH}_2=\text{C}<$ notably the following may be incorporated in the manufacture of the articles in question, namely, vinyl esters, ethers and halides and their substitution products. As examples of these

substances the following may be mentioned, vinyl acetate, propionate, chloracetate, benzoate, vinyl chloride or its substitution products such as chlorstyrole, methyl styrole, and also methyl-, ethyl-, butyl-, chlorethyl-, vinyl ether or vinyl methyl ketone.

Insofar as these substances yield solid polymerisation products they can be employed singly or mixtures of the substances may be employed and in either case with or without additional substances. Polymerisation products which are too hard can be brought to the desired elasticity and softness by means of softening agents. Liquid and semi solid polymerisation products can serve inter alia as softening agents, other examples of which are given below. Moreover the strength of the products can be improved by additions of cellulose ester or ether.

A very satisfactory mixture is for example a mixture of methacrylic acid methyl ester and acrylic acid iso-amyl ester. A polymerisation product of considerable tenacity is obtained by polymerising together a mixture of acrylic acid nitrile and acrylic acid methyl ester approximately in the proportion 1:3 but the strength of the ester polymerisation product is improved by even smaller quantities of acrylic acid nitrile. Also acrylic acid amide can be employed.

As stated the polymerised acrylic and methacrylic compounds may be employed with additional substances whereby their properties may be modified. As examples of additional substances the following may be mentioned:—softening agents such for example as phthalic, tartaric, adipic, stearic and phosphoric acid esters; ethers and esters of polyvalent alcohols such for example as diethylene glycol ethyl ether or acetone; mineral and vegetable oils such as linseed oil or castor oil; artificial and natural resins such as copals, colophony; artificial and natural caoutchouc

in small quantities; urea- and phenol-formaldehyde condensation products; para-toluene sulpho amido resins, resins from polyvalent acids and alcohols and the like; also cellulose compounds such as nitro or acetyl cellulose, cellulose ethers such as methyl, ethyl, or benzyl cellulose; basic substances such as urea, guanidine and their derivatives; filling materials such as talcum; colouring matters such for example as those of the anthraquinone series; and antiseptic agents. These substances can be added to the acrylic or methacrylic compounds at any suitable stage in the manufacture of the articles and before, during or after polymerisation and with or without solvents.

The polymerisation itself may be effected at any suitable stage in the manufacture of the articles and either, before or after the articles are formed or gradually or in stages during the forming of the articles. Moreover the polymerisation can be carried out by the usual methods such as by the aid of heat, light and/or catalysts and in the presence or absence of solvents or diluents or in the form of emulsions, according to the substance to be polymerised and the polymerisation products to be obtained. For example it has been found that of the different stages of polymerisation of the polymerisation products the highly viscous products having a viscosity of about 40 and more degrees Engler in 10% ethyl acetate solution, are very favourable. Such products are obtained above all if the polymerisation is carried out in the absence of solvent or in the presence of little solvent as well as with the use of as small as possible quantities of catalysts. A sufficiently highly viscous polymerised acrylic acid methyl ester is obtained for example if the polymerisation is carried out in a 60% acetic ester solution at about 80° C. with addition of about 0.01% benzoyl superoxide. In the production of polymerised highly viscous methacrylic acid esters it is best to work without solvent.

As solvents and diluents the following inter alia may be employed water, aromatic and aliphatic hydrocarbons such as benzene or benzene; chlorinated hydrocarbons such as ethylene chloride, trichlorethylene, chloroform, chlorobenzene, dichlorobenzene and so forth; esters such as methyl acetate, ethyl acetate, butyl acetate, cyclo-hexanol acetate and so forth; ethers such as ethyl ether, dioxane and so forth; alcohols such as methanol, ethyl alcohol, butanol, benzyl alcohol; ketones such as acetone, methyl ethyl ketone, cyclo-hexanone, methyl cyclo-

hexanone and the like.

The formation of the articles in question can be effected by the most varied methods for example by dipping, squirting, drawing or moulding. The dipping method is preferably carried out by dipping a form body member of the usually employed materials such for example as artificial resin or caoutchouc, or glass, porcelain or metal and especially tinned copper or non-rusting steel, into a solution of a polymerisation product or mixture of polymerisation products with or without additional substances, allowing the form member to remain for a short time in the solution and then gradually and uniformly drawing it up out of the solution, whereby the latter adheres to the walls of the form member in the form of a film. After drawing out, the form member is preferably rotated in order to obtain uniform flow of solution to the point of the form member. After removal of the solvent which can be effected by evaporation or hanging up in water, a film coating remains the thickness of which depends upon the conditions of production such as concentration, viscosity and temperature of solution, speed of drawing out of the solution, regulation of the evaporation, number of times dipped, and so forth and can be suitably varied as described by varying these different factors. For example it is possible to produce films of 0.01 mm. and even less thickness. Also it is possible to effect repeated dipping in different solutions and thereby to combine valuable properties of different substances. Moreover it has been found advantageous in the case of repeated dippings to wet the form members before each dipping with a high boiling point solvent or a low percentage solution of polymerisation product or mineral oil.

In order to produce a reinforced edge to the articles, the film is rolled back somewhat to the desired thickness while it is still in a sticky condition. In order to secure better adhesion a small quantity of adhesive, preferably a dilute solution of a polymerisation product can be painted on from time to time. Also reinforcing rings made from the substance sold under the Registered Trade Mark "Plexigum" or any other suitable material for example rubber can be rolled into the edge. The coating is then sprinkled with powder inside and out and if desired dried in vacuo.

The films of polymerisation products of lower viscosity are in general more difficultly rollable or entirely unrollable. It has been found that the highly viscous products possess good rolling properties and that by sprinkling with powder, meal,

flour or the like of various kinds for example of diatomaceous earth, chalk, gypsum, lycopodium, maize- or rice starch, or wheaten flour, the rollability can be still further improved. In the case of polymerisation products to which the powder does not properly adhere, adhesion can be promoted either by moistening the polymerisation product with a small quantity of solvent and then powdering or by sprinkling on the powder at a higher temperature.

Instead of employing a dipping method it is also possible to employ a squirting method. In this case the solution may be forced through a round nozzle in tubular form, and the solvent is evaporated for example in a hot chamber. The tubes are cut off to the required lengths, segments are cut at the ends and the points or flaps are folded together hemispherically and caused to adhere together.

Further it is possible to manufacture articles of the kind set forth by blowing a solution of one or more of the said polymerisation products, if desired into forms or moulds and removing the solvent. The solution may be employed warm and/or it may be blown with warm air. After most of the solvent has been evaporated the mould can be suspended in water for a time after which the body formed is removed. Instead of employing solutions, films can be employed in a similar manner to that employed in the working up of celluloid.

Articles of the kind described can also be manufactured by drawing a ready prepared film of a polymerisation product or products over a mandrel and stretching it at an elevated temperature. The stretched film is held in position and kept warm until it has completely adapted itself to the required form and retains this form upon being removed.

In order that the invention may be well understood the following specific examples will be given by way of illustration only:—

EXAMPLE 1.

A smooth metal or porcelain tube of 80 mm. diameter and 800 mm. in length and closed at the end in the form of a hemisphere is dipped into a 12% solution of highly viscous polymerised acrylic acid methyl ester in ethyl acetate (viscosity 120° Engler in 10% solution) and after about 1 minute it is uniformly withdrawn, with a speed of about 8 cms. per minute. After the last drops of solution have fallen off, which operation is assisted by rotating the tube, the tube is suspended for about 15 minutes in water. Thereupon the film coating formed on the tube is drawn off and powdered inside and

out with rice flour. After drying a resistant flexible sack results.

EXAMPLE 2.

A form member of hard caoutchouc is dipped into a 12% solution of 20 parts of highly viscous polymerised methacrylic acid ethyl ester (viscosity 250° Engler in 10% ethyl acetate solution) and 10 parts of methylglycol phthalate and 1 part of castor oil in benzene, and uniformly withdrawn during the course of 8 minutes. After removal of the solvent and drying a flexible sack of 0.05 mm. wall thickness and of good strength is obtained. It is sprinkled with potato flour and rolled up.

EXAMPLE 3.

A 20% solution of 95 parts of polymerised acrylic acid methyl ester, which contains 5 parts of nitrocellulose in ethyl acetate out with 10% butanol is mixed with 1 part of castor oil and 5 parts of acetone and employed as in Example 1. A sack of the like of good quality and strength is obtained.

EXAMPLE 4.

2 parts of triresyl phosphate are added to a 20% solution in acetone of 3 parts polyacrylic methyl ester and 2 parts of polyacrylic acid nitrile which have been polymerised in common together and a glass or metal tube is slowly drawn through the solution. After evaporating the solvent the tube is dipped into a 2% mineral oil solution in monochlorobenzene and again passed through the acetone solution. This process is repeated several times so that finally a strong film coating is produced and this, after soaking in water can easily be drawn off and yields a solid durable ampulla.

EXAMPLE 5.

A mixture of 50 parts of polymerised acrylic acid ethyl ester and 88 parts monochlorobenzene is pressed at about 80–100° C. under 30–40 atmospheres pressure through a ring nozzle into a heated chamber and the solvent evaporated. The tube so formed is then divided up in the manner described heretofore and at one end divided into segments by incisions. These are formed by a spherical curvature and joined together by adhesion preferably in a warm state.

EXAMPLE 6.

A prepared film of 92 parts polymerised acrylic acid methyl ester and 8 parts of methylglycolphthalate prepared by pouring out and evaporating a 25% ethyl acetate solution, is drawn over a mandrel and held there for a few hours at 40–50° C. until the film has adapted itself to the shape of the mandrel and will retain this form even upon removal. In this manner, tests of good quality can be prepared.

EXAMPLE 7.

A 12% solution in benzene of 86 parts of methacrylic acid iso-amyl ester, 10 parts of adipic acid cyclo-hexyl ester and 4 parts of mineral oil of specific gravity 0.88, is employed in the manner described in Example 1.

EXAMPLE 8.

A mixture of 20 parts acrylic acid propyl ester and 60 parts of vinyl acetate, prepared by a common polymerisation and 20 parts of methylglycol phthalate is heated to 100–120° C. and pressed into a teat mould heated to this temperature. After cooling the mould is opened and a teat of good durability is obtained.

EXAMPLE 9.

As shown by the following, mixtures of different polymerisation products can be employed. A mixture of 1 part of styrole, 2 parts vinyl acetate, 8 parts of acrylic acid methyl ester and 1 part of methacrylic acid methyl ester is polymerised with addition of 0.1% benzoyl superoxide, 75 parts of this mixed polymerisation product are dissolved with 25 parts of diamyl phthalate in ethylene chloride to make a 20% solution and employed as described in any one of the foregoing examples for the production of articles of the kind described.

EXAMPLE 10.

90 parts of acrylic acid iso-propyl ester and 10 parts of acrylic acid are poly-

merised in common. 90 parts of this polymerised mixture are dissolved to a strength of 20% in a mixture of ethyl acetate and butanol mixed in the proportion 4:1 and 5 parts of phenol formaldehyde condensation product in the form of a 50% solution in acetone are added and the solution is employed as in Examples 1 to 8. An article of very great strength is produced.

EXAMPLE 11.

By dipping a form member into a solution prepared as described in Example 4 a film coating is produced. This is dipped for a short time in a solution of 2 parts of mineral oil in 98 parts of cyclohexanone and a layer is then produced by dipping in a solution of highly viscous polymerised acrylic acid methyl ester produced according to Example 1. After drying a satisfactory sack is obtained.

Whilst in the foregoing some preferred examples have been given as illustrative of the manner of carrying out this invention it is to be understood that various modifications may be made without departing from the scope thereof.

Dated this 13th day of September, 1932.

For the Applicant,

FRANK B. DEHN & Co.,

Chartered Patent Agents,

Kingsway House, 103, Kingsway,
London, W.C.2.

COMPLETE SPECIFICATION (AMENDED).**Improvements in or relating to the Manufacture of Hollow Flexible Articles.**

I, FRANK BERNHARD DEHN, M.Sc., Ph.D., A.I.C., Chartered Patent Agent, a British Subject, of Kingsway House, 103, Kingsway, London, W.C. 2, do hereby declare the nature of this invention (which has been communicated to me by Röhm & Haas Aktiengesellschaft, a Joint Stock Company organised under German Law, of Weiterstädterstrasse 42, Darmstadt, Germany), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to improvements in or relating to the manufacture of hollow, highly flexible articles such as tubes, finger stalls, ampulæ, teats or bulbs. Such articles have in general been made of rubber.

It has previously been proposed to manufacture tubes from polymerised vinyl alcohols.

According to the present invention

articles of the kind described are made of solid elastic and flexible compositions comprising one or more wholly or partially polymerised acrylic and/or methacrylic acid esters and/or nitriles or their halogen substitution products.

In particular there may be mentioned the methyl, ethyl, propyl, amyl, phenyl and benzyl esters and their halogen substitution products such as chloracrylic acid methyl ester.

These products are stable as regards their strength, have good extensibility and resistance to tearing and the special elasticity required for the manufacture of finger stalls and the like which must make a good fit without producing hurtful pressure through being pressed or drawn on.

In addition to the compounds mentioned above, other substances containing the group $\text{CH}_2=\text{C}<$ notably the following may be incorporated in the manufac-

ture of the articles in question, namely, vinyl esters, ethers and halides and their substitution products. As examples of these substances the following may be mentioned, vinyl acetate, propionate, chloracetate benzoate, vinyl chloride or its substitution products such as chlorstyrol, methyl styrol and also methyl-, ethyl-, butyl-, chlorethyl-, vinyl ether or vinyl methyl ketone.

The articles in question are particularly advantageously made from polymerisation products containing besides one or more of the esters in question, also a quantity, preferably at least 20% of acrylic acid nitrile. More particularly a polymerisation product comprising acrylic acid ethyl ester with about 80% of acrylic acid nitrile is a satisfactory and not dangerously inflammable material. Polymerisation products containing acrylic acid nitrile are in the main insoluble in most of the usual solvents and show a notably slight tendency to swell. This combination of properties renders such compositions particularly suitable for the manufacture of tubes or the like intended to come in contact with liquid fuels or mixtures thereof such for example as benzine, benzene, petrol, alcohol and the like. The quantity of the nitrile employed may be varied within wide limits but it should be noted that the presence of the nitrile in the mixture of polymers is essential for obtaining the special effects referred to.

In the case of these mixed polymers it may be advisable to heat them for some time to temperatures above 100° C., preferably to from 150°—200° C. and if desired under increased pressure. The solubility and the liability to swell in solvents are still further reduced by this treatment.

Insofar as these substances yield solid polymerisation products they can be employed singly or mixtures of the substances may be employed and in either case with or without additional substances.

Some of the polymerisation products such as the ethyl, propyl, butyl, isobutyl and amyl esters of polyacrylic acid and the amyl ester of polymethacrylic acid possess very great softness and flexibility at ordinary temperatures and also even at low temperatures so that they may if desired be used alone for the manufacture of the articles in question.

Polymerisation products which alone are too hard for these purposes such for example as polymethacrylic acid esters of alcohols with up to four carbon atoms, are used in conjunction with suitable softening agents. Soft polymerisation products such as those set forth above, may

be employed as softening agents. It is to be understood however that if desired softening agents may be employed with the soft polymerisation products.

The use of soft polymerisation products as softening agents is of advantage in those cases where hardening occurs in course of time when ordinary softening agents are used by reason perhaps of the softening agents being removed by solvents or at higher temperatures.

The strength of the products may be improved by additions of cellulose esters or ethers.

A very satisfactory mixture is for example a mixture of methacrylic acid methyl ester and acrylic acid iso-amyl ester. A polymerisation product of considerable tenacity is obtained by polymerising together a mixture of acrylic acid nitrile and acrylic acid methyl ester approximately in the proportion 1:3, but the strength of the ester polymerisation product is improved by even smaller quantities of acrylic acid nitrile. Also acrylic acid amide can be employed.

As stated, the polymerised acrylic or methacrylic compounds may be employed with additional substances whereby their properties may be modified. As examples of additional substances the following may be mentioned.—softening agents, such for example as phthalic, tartaric, adipic, stearic and phosphoric acid esters; ethers and esters of polyvalent alcohols such for example as diethylene glycol ethyl ether or acetin; mineral and vegetable oils such as linseed oil or castor oil, artificial and natural resins such as copals, colophony; artificial and natural caoutchouc in small quantities, urea and phenol-formaldehyde condensation products; para toluene sulphonamide resins, resins from polyvalent acids and alcohols and the like; also cellulose compounds such as nitro or acetyl cellulose, cellulose ethers such as methyl, ethyl or benzyl cellulose, basic substances such as urea, guanidine and their derivatives; filling materials such as talcum or kaolin; colouring matters such for example as those of the anthraquinone series; and antiseptic agents. Moreover, other organic or inorganic substances, such for example as zinc stearate, lamp-black, fats, waxes and the like can be added to or mixed with the other constituents if desired. These substances can be added to the said acrylic or methacrylic compounds at any suitable stage in the manufacture of the articles and before, during or after polymerisation and with or without solvents.

The polymerisation itself may be effected

at any suitable stage in the manufacture of the articles and either before or after the articles are formed or gradually or in stages during the forming of the articles. Moreover, the polymerisation can be carried out by the usual methods such as by the aid of heat, light and/or catalysts and in the presence or absence of solvents or diluents or in the form of emulsions, and especially aqueous dispersions according to the substance to be polymerised and the polymerisation products to be obtained. For example, it has been found that of the different stages of polymerisation of the polymerisation products the highly viscous products having a viscosity of about 40 and more degrees Engler in 10% ethyl acetate solution, are very favourable. Such products are obtained above all if the polymerisation is carried out in the absence of solvent or in the presence of little solvent as well as with the use of as small as possible quantities of catalysts. A sufficiently highly viscous polymerised acrylic acid methyl ester is obtained, for example if the polymerisation is carried out in a 60% acetic ester solution at about 80° C. with addition of about 0.01% benzoyl peroxide. In the production of polymerised highly viscous methacrylic acid esters it is best to work without solvent.

As solvents and diluents the following, inter alia, may be employed, water, aromatic and aliphatic hydrocarbons such as benzene or benzine, chlorinated hydrocarbons such as ethylene chloride, trichlorethylene, chloroform, chlorobenzene, dichlorobenzene and so forth; esters such as methyl acetate, ethyl acetate, butyl acetate, cyclohexanol acetate, and so forth, ethers such as ethyl ether, dioxane and so forth; alcohols such as methanol, ethyl, alcohol, butanol, benzyl alcohol; ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl cyclohexanone and the like.

The formation of the articles in question can be effected by the most varied methods for example by dipping, squirting, drawing or moulding. The dipping method is preferably carried out by dipping a form body member of the usually employed materials such, for example, as artificial resin or caoutchouc, or glass, porcelain or metal and especially tinned copper or non-rusting steel, into a solution of a polymerisation product or mixture of polymerisation products with or without additional substances allowing the form member to remain for a short time in the solution and then gradually and uniformly drawing it up out of the solution, whereby the latter adheres to the

walls of the form member in the form of a film. After drawing out, the form member is preferably rotated in order to obtain uniform flow of solution to the point of the form member. After removal of the solvent which can be effected by evaporation or hanging up in water, a film coating remains the thickness of which depends upon the conditions of production such as concentration viscosity and temperature of solution, speed of drawing out of the solution, regulation of the evaporation, number of times dipped, and so forth and can be suitably varied as desired by varying these different factors. For example, it is possible to produce films of 0.01 mm. and even less thickness. Also it is possible to effect repeated dipping in different solutions and thereby to combine valuable properties of different substances. Moreover, it has been found advantageous in the case of repeated dippings to wet the form members before each dipping with a high boiling point solvent or a low percentage solution of polymerisation product or mineral oil.

In order to produce a reinforced edge to the articles, the film is rolled back somewhat to the desired thickness while it is still in a sticky condition. In order to secure better adhesion a small quantity of adhesive, preferably a dilute solution of a polymerisation product can be painted on from time to time. Also reinforcing rings made from the substance sold under the Registered Trade Mark "Plexigum" or any other suitable material for example, rubber, can be rolled into the edge. The coating is then sprinkled with powder inside and out and if desired dried in vacuo.

The films of polymerisation products of lower viscosity are in general more difficultly rollable or entirely unrollable. It has been found that the highly viscous products possess good rolling properties and that by sprinkling with powder, meal, flour or the like of various kinds for example of diatomaceous earth, chalk, gypsum, lycopodium, maize or rice starch, or wheaten flour the rollability can be still further improved. In the case of polymerisation products to which the powder does not properly adhere, adhesion can be promoted either by moistening the polymerisation product with a small quantity of solvent and then powdering or by sprinkling on the powder at a higher temperature.

Instead of employing a dipping method it is also possible to employ a squirting method. In this case a solution may be forced through a round nozzle in tubular form, and the solvent is evaporated for

example in a hot chamber. The tubes are cut off to the required lengths, segments are cut at the ends and the points or flaps are folded together hemispherically and caused to adhere together.

5 The squirting method can also be carried out without the addition of solvents, especially if such substances as talcum and cellulose esters are added to the polymers (see Example 14).

10 Further it is possible to manufacture articles of the kind set forth by blowing a solution of one or more of the said polymerisation products, if desired into forms or moulds and removing the solvent. The solution may be employed warm and/or it may be blown with warm air. After most of the solvent has been evaporated the mould can be suspended in water for a time, after which the body formed is removed. Instead of employing solutions, films can be employed in a similar manner to that employed in the working up of celluloid.

25 Articles of the kind described can also be manufactured by drawing a ready prepared film of a polymerisation product or products over a mandrel and stretching it at an elevated temperature. The stretched film is held in position and kept warm until it has completely adapted itself to the required form and retains this form upon being removed.

30 In order that the invention may be well understood the following specific examples will be given by way of illustration only:—

EXAMPLE 1.

40 A smooth metal or porcelain tube of 30 mm. diameter and 800 mm. in length and closed at the end in the form of a hemisphere is dipped into a 12% solution of highly viscous polymerised acrylic acid methyl ester in ethyl acetate (viscosity 120° Engler in 10% solution) and after 45 about 1 minute it is uniformly withdrawn, with a speed of about 8 cms. per minute. After the last drops of solution have fallen off which operation is assisted by 50 rotating the tube, the tube is suspended for about 15 minutes in water. Thereupon the film coating formed on the tube is drawn off and powdered inside and out with rice flour. After drying a resistant 55 flexible sack results.

EXAMPLE 2.

60 A form member of hard caoutchouc is dipped into a 12% solution of 20 parts of highly viscous polymerised methacrylic acid ethyl ester (viscosity 250° Engler in 10% ethyl acetate solution) and 10 parts of methylglycol phthalate and 1 part of castor oil in benzene and uniformly withdrawn during the course of 3 minutes. 65 After removal of the solvent and drying a

flexible sack of 0.5 mm. wall thickness and of good strength is obtained. It is sprinkled with potato flour and rolled up.

EXAMPLE 3.

70 A 20% solution of 95 parts of polymerised acrylic acid methyl ester, which contains 5 parts of nitrocellulose in ethyl acetate cut with 10% butanol is mixed with 1 part of castor oil and 5 parts of acetin and employed as in Example 1. 75 A sack or the like of good quality and strength is obtained.

EXAMPLE 4.

80 2 parts of tricresyl phosphate are added to a 20% solution in acetone of 8 parts polyacrylic methyl ester and 2 parts of polyacrylic acid nitrile which have been polymerised in common together and a glass or metal tube is slowly drawn through the solution. After evaporating 85 the solvent the tube is dipped into a 2% mineral oil solution in monochlorobenzene and again passed through the acetone solution. This process is repeated several times so that finally a strong film coating is produced and this, after soaking in water can easily be drawn off and yields a solid durable ampulla.

EXAMPLE 5.

95 A mixture of 50 parts of polymerised acrylic acid ethyl ester and 38 parts monochlorobenzene is pressed at about 80–100° C. under 30–40 atmospheres pressure through a ring nozzle into a heated chamber and the solvent eva- 100 porated. The tube so formed is then divided up in the manner described heretofore and at one end divided into segments by incisions. These are formed to a spherical curvature and joined together 105 by adhesion preferably in a warm state.

EXAMPLE 6.

A prepared film of 92 parts polymerised acrylic acid methyl ester and 8 parts of methylglycolphthalate prepared by pour- 110 ing out and evaporating a 25% ethyl acetate solution, is drawn over a mandrel and held there for a few hours at 40–50° C. until the film has adapted itself to the shape of the mandrel and will retain this 115 form even upon removal. In this manner, teats of good quality can be prepared.

EXAMPLE 7.

A 12% solution in benzene of 86 parts of methacrylic acid iso-amyl ester, 10 120 parts of adipic acid cyclo hexyl ester and 4 parts of mineral oil of specific gravity 0.88, is employed in the manner described in Example 1.

EXAMPLE 8.

125 A mixture of 20 parts acrylic acid propyl ester and 60 parts of vinyl acetate, prepared by a common polymerisation and 20 parts of methylglycol phthalate is heated to 100–120° C. and pressed into a 130

example in a hot chamber. The tubes are cut off to the required lengths, segments are cut at the ends and the points or flaps are folded together hemispherically and

5 caused to adhere together.
The squirting method can also be carried out without the addition of solvents, especially if such substances as talcum and cellulose esters are added to the polymers (see Example 14).

10 Further it is possible to manufacture articles of the kind set forth by blowing a solution of one or more of the said polymerisation products, if desired into forms or moulds and removing the solvent. The solution may be employed warm and/or it may be blown with warm air. After most of the solvent has been evaporated the mould can be suspended in water for a time, after which the body formed is removed. Instead of employing solutions, films can be employed in a similar manner to that employed in the working up of celluloid.

25 Articles of the kind described can also be manufactured by drawing a ready prepared film of a polymerisation product or products over a mandrel and stretching it at an elevated temperature. The stretched film is held in position and kept warm until it has completely adapted itself to the required form and retains this form upon being removed.

30 In order that the invention may be well understood the following specific examples will be given by way of illustration only:—

EXAMPLE 1.

40 A smooth metal or porcelain tube of 30 mm. diameter and 800 mm. in length and closed at the end in the form of a hemisphere is dipped into a 12% solution of highly viscous polymerised acrylic acid methyl ester in ethyl acetate (viscosity 120° Engler in 10% solution) and after about 1 minute it is uniformly withdrawn, with a speed of about 8 cms. per minute. After the last drops of solution have fallen off which operation is assisted by rotating the tube, the tube is suspended for about 15 minutes in water. Thereupon the film coating formed on the tube is drawn off and powdered inside and out with rice flour. After drying a resistant flexible sack results.

EXAMPLE 2.

60 A form member of hard caoutchouc is dipped into a 12% solution of 20 parts of highly viscous polymerised methacrylic acid ethyl ester (viscosity 250° Engler in 10% ethyl acetate solution) and 10 parts of methylglycol phthalate and 1 part of castor oil in benzene and uniformly withdrawn during the course of 3 minutes. After removal of the solvent and drying a

flexible sack of 0.5 mm. wall thickness and of good strength is obtained. It is sprinkled with potato flour and rolled up.

EXAMPLE 3.

A 20% solution of 95 parts of polymerised acrylic acid methyl ester, which contains 5 parts of nitrocellulose in ethyl acetate cut with 10% butanol is mixed with 1 part of castor oil and 5 parts of acetin and employed as in Example 1. A sack or the like of good quality and strength is obtained.

EXAMPLE 4.

2 parts of tricresyl phosphate are added to a 20% solution in acetone of 8 parts polyacrylic methyl ester and 2 parts of polyacrylic acid nitrile which have been polymerised in common together and a glass or metal tube is slowly drawn through the solution. After evaporating the solvent the tube is dipped into a 2% mineral oil solution in monochlorobenzene and again passed through the acetone solution. This process is repeated several times so that finally a strong film coating is produced and this, after soaking in water can easily be drawn off and yields a solid durable ampulla.

EXAMPLE 5.

A mixture of 50 parts of polymerised acrylic acid ethyl ester and 38 parts monochlorobenzene is pressed at about 80–100° C. under 30–40 atmospheres pressure through a ring nozzle into a heated chamber and the solvent evaporated. The tube so formed is then divided up in the manner described heretofore and at one end divided into segments by incisions. These are formed to a spherical curvature and joined together by adhesion preferably in a warm state.

EXAMPLE 6.

A prepared film of 92 parts polymerised acrylic acid methyl ester and 8 parts of methylglycolphthalate prepared by pouring out and evaporating a 25% ethyl acetate solution, is drawn over a mandrel and held there for a few hours at 40–50° C. until the film has adapted itself to the shape of the mandrel and will retain this form even upon removal. In this manner, tests of good quality can be prepared.

EXAMPLE 7.

A 12% solution in benzene of 86 parts of methacrylic acid iso-amyl ester, 10 parts of adipic acid cyclo hexyl ester and 4 parts of mineral oil of specific gravity 0.88, is employed in the manner described in Example 1.

EXAMPLE 8.

A mixture of 20 parts acrylic acid propyl ester and 60 parts of vinyl acetate, prepared by a common polymerisation and 20 parts of methylglycol phthalate is heated to 100–120° C. and pressed into a

example in a hot chamber. The tubes are cut off to the required lengths, segments are cut at the ends and the points or flaps are folded together hemispherically and caused to adhere together.

The squirting method can also be carried out without the addition of solvents, especially if such substances as talcum and cellulose esters are added to the polymers (see Example 14).

Further it is possible to manufacture articles of the kind set forth by blowing a solution of one or more of the said polymerisation products, if desired into forms or moulds and removing the solvent. The solution may be employed warm and/or it may be blown with warm air. After most of the solvent has been evaporated the mould can be suspended in water for a time, after which the body formed is removed. Instead of employing solutions, films can be employed in a similar manner to that employed in the working up of celluloid.

Articles of the kind described can also be manufactured by drawing a ready prepared film of a polymerisation product or products over a mandrel and stretching it at an elevated temperature. The stretched film is held in position and kept warm until it has completely adapted itself to the required form and retains this form upon being removed.

In order that the invention may be well understood the following specific examples will be given by way of illustration only:—

EXAMPLE 1.

A smooth metal or porcelain tube of 30 mm. diameter and 800 mm. in length and closed at the end in the form of a hemisphere is dipped into a 12% solution of highly viscous polymerised acrylic acid methyl ester in ethyl acetate (viscosity 120° Engler in 10% solution) and after about 1 minute it is uniformly withdrawn, with a speed of about 8 cms. per minute. After the last drops of solution have fallen off which operation is assisted by rotating the tube, the tube is suspended for about 15 minutes in water. Thereupon the film coating formed on the tube is drawn off and powdered inside and out with rice flour. After drying a resistant flexible sack results.

EXAMPLE 2.

A form member of hard caoutchouc is dipped into a 12% solution of 20 parts of highly viscous polymerised methacrylic acid ethyl ester (viscosity 250° Engler in 10% ethyl acetate solution) and 10 parts of methylglycol phthalate and 1 part of castor oil in benzene and uniformly withdrawn during the course of 3 minutes. After removal of the solvent and drying a

flexible sack of 0.5 mm. wall thickness and of good strength is obtained. It is sprinkled with potato flour and rolled up.

EXAMPLE 3.

A 20% solution of 95 parts of polymerised acrylic acid methyl ester, which contains 5 parts of nitrocellulose in ethyl acetate cut with 10% butanol is mixed with 1 part of castor oil and 5 parts of acetin and employed as in Example 1. A sack or the like of good quality and strength is obtained.

EXAMPLE 4.

2 parts of tricresyl phosphate are added to a 20% solution in acetone of 8 parts polyacrylic methyl ester and 2 parts of polyacrylic acid nitrile which have been polymerised in common together and a glass or metal tube is slowly drawn through the solution. After evaporating the solvent the tube is dipped into a 2% mineral oil solution in monochlorobenzene and again passed through the acetone solution. This process is repeated several times so that finally a strong film coating is produced and this, after soaking in water can easily be drawn off and yields a solid durable ampulla.

EXAMPLE 5.

A mixture of 50 parts of polymerised acrylic acid ethyl ester and 38 parts monochlorobenzene is pressed at about 80—100° C. under 30—40 atmospheres pressure through a ring nozzle into a heated chamber and the solvent evaporated. The tube so formed is then divided up in the manner described heretofore and at one end divided into segments by incisions. These are formed to a spherical curvature and joined together by adhesion preferably in a warm state.

EXAMPLE 6.

A prepared film of 92 parts polymerised acrylic acid methyl ester and 8 parts of methylglycolphthalate prepared by pouring out and evaporating a 25% ethyl acetate solution, is drawn over a mandrel and held there for a few hours at 40—50° C. until the film has adapted itself to the shape of the mandrel and will retain this form even upon removal. In this manner, teats of good quality can be prepared.

EXAMPLE 7.

A 12% solution in benzene of 86 parts of methacrylic acid iso-amyl ester, 10 parts of adipic acid cyclo hexyl ester and 4 parts of mineral oil of specific gravity 0.88, is employed in the manner described in Example 1.

EXAMPLE 8.

A mixture of 20 parts acrylic acid propyl ester and 60 parts of vinyl acetate, prepared by a common polymerisation and 20 parts of methylglycol phthalate is heated to 100—120° C. and pressed into a